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FACTORS AFFECTING THE PHOTOCHEMICAL TREATMENT OF HAZARDOUS WASTE

by

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Abstract

The photochemical treatment of hazardous waste can be optimized by taking into account several factors that influence the rates of photochemical reactions. Physical factors that facilitate photochemical treatment include: (1) maximizing the irradiated surface to volume ratio of the system, (2) selecting a light source with a spectrum that strongly overlaps the absorption spectrum of the chromophore, (3) vigorously mixing the reactants. Although hazardous wastes are degraded by the direct absorption of light, the overall rate of light-induced reactions can usually be accelerated by adding to the treatment system various dissolved or particulate substances that, upon light absorption, produce reactive excited states or free radical intermediates that also react with the waste. Examples of such additives include ozone, peroxides, semiconducting metal oxides, such as titanium dioxide, and various organic photosensitizers that efficiently photoproduce excited triplet states.

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INTRODUCTION

Treatment of wastes by photochemical reaction differs from usual chemical techniques in that the prime reactant, light, somehow must be added to the system, which is usually contained in a glass vessel or outdoor treatment area. The light source may be the sun or a lamp of some type.

Photochemical treatment can be optimized by taking into account various factors that influence the rates of photoreactions:

*Light intensity (or scalar irradiance)

*Light spectrum

*Spectral response of the photochemical system

-Electronic absorption spectrum and concentration of chemical that initiates photoreaction

-Overall quantum yield

*Mixing

The overall quantum yield is the fraction of absorbed light at wavelength λ that results in the photoreaction of some substrate. The rate of a photochemical reaction is wavelength dependent. For polyatomic organic compounds in solution this dependence is mainly attributable to variations in the specific light absorption rate with wavelength (1). Overall quantum yields are also dependent on wavelength, but this dependence is usually small in solution.

The photoreaction rate for a given treatment system can be optimized in several ways (1). First, and most important, the light source and material of the reaction cell through which the light passes should be selected to maximize the overlap of the electronic absorption spectrum of the chromophore and the spectrum of the light that enters the reaction medium. Finlayson-Pitts and Pitts (2) and Zepp (1) discuss various lamps that are commonly used. Second, retardation by light attenuation effects can be minimized by maximizing the surface area to volume ratio of the photoreactor. Third, especially in systems where all of the incident light is absorbed, it is important that the reaction mixture be well mixed to avoid transport limitations on the conversion rate.

Two general types of photoreactions can be used in photochemical treatment. Direct photolysis involves light absorption by the substrate followed by chemical reaction of the substrate in its electronically excited state. Direct photolysis is the only pathway for photoreaction in a reaction medium that is transparent to the incident light. Indirect photoreactions involve chemical reaction of a substrate that is induced through light absorption by another substance in the system. Indirect photoreactions are mediated by excited states of photosensitizers, by free radicals of various types, and by other short-lived, reactive intermediates. In principle, direct and indirect photoreactions may occur in parallel in a treatment system.

General approaches have been developed to compute light-

induced reaction rates as a function of system composition, spectral irradiance of the light source, and quantum yields (2, 3). For example, Simmons and Zepp (4) have successfully used overall quantum yields for direct photoreactions of a series of nitroaromatic compounds to compute their photoreaction rate constants in sunlight (Figure 1). Applications of direct photoreactions and several types of indirect photoreactions to treatment of hazardous waste are discussed in the balance of this presentation.

DIRECT PHOTOREACTIONS

A wide variety of reactions occur upon direct absorption of light by hazardous wastes. For general background on this subject, the book by Turro (5) is particularly useful for organic photoreactions as are books by Balzani and Carassiti (6) and Adamson and Fleischauer (7) for inorganic photoreactions. Xenobiotic photoproducts are more specifically described by Crosby and co-workers (8) and Sundstrom and Ruzo (9) among many others. At elevated temperatures with high intensity ultraviolet light, organic compounds in water can be extensively mineralized (10). Moreover, the products of direct photoreactions of biologically refractory xenobiotics are sometimes considerably more susceptible to biodegradation than the xenobiotic itself (11).

Table 1 summarizes direct photolysis half-lives that have been observed for different types of hazardous wastes using sunlight as the light source. These data show that many notorious pollutants, such as pentachlorophenol, polycyclic aromatic hydrocarbons, and 2,3,7,8-tetrachlorodibenzodioxin, are

highly susceptible to photolysis. All of these compounds absorb only the ultraviolet portion of ground-level sunlight.

Generally, the overall quantum yields, reaction products, and, to a lesser extent, the electronic absorption spectra are very sensitive to the nature of the reaction medium. The nearly 20-fold enhancement in the quantum yield for direct photolysis of TCDD in hexane compared to water-acetonitrile (90:10) provides a good example of such a medium effect (12). Because organic compounds usually are much more soluble in organic solvents than in water, most past studies have focused on direct photoreactions in organic media (5,8,9). These studies may be pertinent to systems in which hydrophobic organic wastes are predominantly partitioned into oil or micellized surfactants. Photoreactions of organic compounds in micelles have been shown to proceed with different rates and products than observed in water (13). In addition to solution phase treatment, direct photolysis also can be used for surface decontamination, as Draper and co-workers (14) have shown in the case of PCB-contaminated surfaces.

Variations in reaction conditions can have important effects on rates and products of direct photoreactions in water. For example, direct photoreactions of ionizable compounds, such as chlorophenols, are often very sensitive to pH (11). The presence of electron donors such as amines (15) or reductants such as sodium borohydride (16) can greatly enhance the overall quantum yields of chlorinated aromatic compounds such as hexachlorobenzene or chlorinated dibenzofurans.

PHOTOSENSITIZED REACTIONS

Photosensitized reactions involve the transfer of electronic energy from an excited sensitizer either directly to the substrate or to dioxygen (5). Energy transfer to dioxygen results in formation of singlet oxygen, an excited form of oxygen that can rapidly oxidize certain xenobiotics. Wilkinson and Brummer (17) have provided an extensive review of singlet oxygen chemistry. Certain dyes, such as rose bengal, eosin, and methylene blue, are particularly effective water-soluble photosensitizers of oxidations involving singlet oxygen. Dye photosensitizers have excellent spectral overlap with sunlight as well as with the light from most lamps. They also efficiently transfer energy to dioxygen to form singlet oxygen. Dyes have been used in solution or chemically-bonded to polymers. Paczkowski and Neckers (18) have reviewed the use of polymer-based photosensitizers. Inexpensive materials such as humic substances, although less efficient than the above-mentioned dyes, also can photosensitize oxygenations of certain pollutants in sunlight (3). Recent research on field applications of this promising treatment technique has been discussed by Eisenberg and co-workers (19).

It is worth noting that singlet oxygen is a selective oxidizing species that reacts rapidly only with certain types of organic compounds such as phenols, furans, sulfides, polycyclic aromatics, and olefins (17). The peroxidic products of singlet oxygen reactions, however, may further decompose into reactive free radicals that can oxidize materials that are unreactive towards singlet oxygen itself.

UV/OZONE OXIDATIONS

The combination of ultraviolet light (<300 nm) and ozone is an effective technique for the oxidation of pollutants in water. In such a system, organic oxidations occur by several potential mechanisms:

(1) Most compounds that have unsaturated chemical bonding, e.g. aromatic hydrocarbons, ketones, and polyenes, absorb the 254 nm light that is used in the UV/ozone procedure. For such compounds, direct photolysis may be an important loss mechanism, although UV light screening by the ozone would greatly reduce the rate of this type of reaction compared to the rate in pure water. In addition to direct photolysis, two other types of processes involving the ozone potentially can result in organic oxidations. These are illustrated by Hoigne and Bader (20) in Figure 2 and discussed below.

(2) Thermal reactions between ozone and certain organics may be an important oxidation pathway in the system (21). Ozone, like singlet oxygen, however, is a highly selective oxidant. Most organic pollutants are not rapidly oxidized by direct reaction with ozone.

(3) Free radicals, produced by photochemical and/or thermal processes in the UV/ozone system, make a major contribution to the organic oxidations that occur. Direct photolysis of ozone in water leads to nearly quantitative production of hydrogen peroxide. Hydrogen peroxide, hydroperoxide ions, or hydroxide ions react with the ozone to produce a potent oxidant, the hydroxyl radical. Direct photolysis of the hydrogen peroxide also contributes to the production of OH radicals. Hydroxyl

radicals react rapidly with most xenobiotics by abstracting hydrogen atoms or by addition to aromatic systems and double bonds. For more detailed discussions of free radical oxidations in the UV/ozone system, the reader is referrred to two excellent papers by Hoigne and Bader (21) and by Peyton and Glaze (22).

SEMICONDUCTOR REACTIONS

Irradiated semiconductors are versatile reagents that show promise for treatment of hazardous wastes. Titanium dioxide has been shown to effectively photocatalyze both reductions of chlorinated organics as well as the oxidation of various other organic chemicals (23-27). For example, Ollis (24) has shown that chloroform is efficiently photomineralized in an aqueous suspension of titanium dioxide exposed to black-light fluorescent lamps (Region III of Figure 3). Chloroform is stable to blacklights in the absence of titanium dioxide (Region I, Figure 3) and no reaction occurs in dark controls (Region II, Figure 3). This type of reaction also can be used to oxidize inorganic wastes, as shown by Frank and Bard (27) and by Carey and Oliver (28). Results of Carey and Oliver (28) using titanium dioxide as photocatalyst for cyanide treatment are shown in Figure 4. Surface-modified titanium dioxide as well as other metal oxides, such as zinc oxide (23), potentially could be used in the photochemical treatment of hazardous wastes.

OTHER POSSIBILITIES

The discussion here is by no means meant to be comprehensive, but rather to provide some indication of the potential of photochemical reactions for treatment of hazardous

wastes. Any substance that efficiently photolyzes to produce reactive free radicals may be useful in photochemical treatment systems. Readily available reagents such as nitrate (29) and humic substances (30) photoreact to form free radicals and thus possibly could be used in such treatment processes. Likewise, treatment processes have been developed that are based on the UV photolysis of hydrogen peroxide to form hydroxyl radicals (31).

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Table 1. Direct photolysis half-lives for various organic chemicals in sunlight (midday, latitiude 40°N).

CHEMICAL	SOLVENT	OVERALL QUANTUM YIELD	SUNLIGHT HALF-LIFE, HRS.	REF.
Pentachloro-phenol	Water	0.014	1.0	11
2,3,7,8-Tetrachloro-dibenzodioxin	Water-Acetonitrile (90:10)	0.0022	52	12
	Hexane	0.049	2	12
2,4,5-Tri-chlorophenol	Water	0.080	0.5	11
Pyrene	Water	0.0022	0.68	32
Anthracene	Water	0.0030	0.75	32
Benzo[a]-pyrene	Water	0.0033	0.54	33

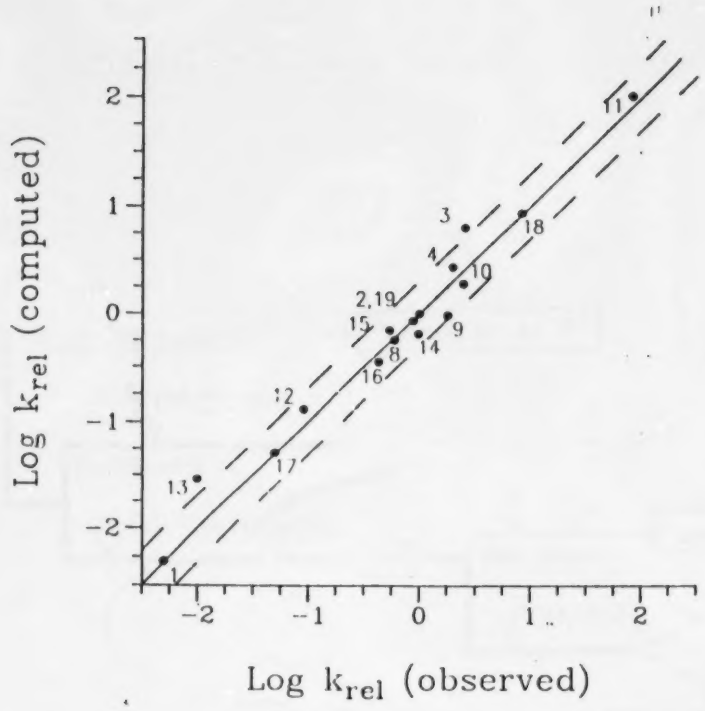

Figure 1. Comparison of sunlight photolysis rate constants for nitroaromatic compounds computed using laboratory data and determined from outdoor experiments. 1, Nitrobenzene; 2, 2-nitrotoluene; 3, 3-nitrotoluene; 4, 4-nitrotoluene; 5, 2-(trifluoromethyl)nitrobenzene; 6, 3-(trifluoromethyl)nitrobenzene; 7, 4-(trifluoromethyl)nitrobenzene; 8, 2-nitro-1,3-xylene; 9, 4-nitro-1,3-xylene; 10, 5-nitro-1,3-xylene; 11, 4-nitro-1,2-xylene; 12, 2,4,6-trifluoronitrobenzene; 13, 1,3-dinitrobenzene; 14, 2,6-dinitrotoluene; 15, 2,4-dinitrotoluene; 16, 2,3-dinitrotoluene; 17, 3,4-dinitrotoluene; 18, 2,5-dinitrotoluene; 4-nitroanisole (4).

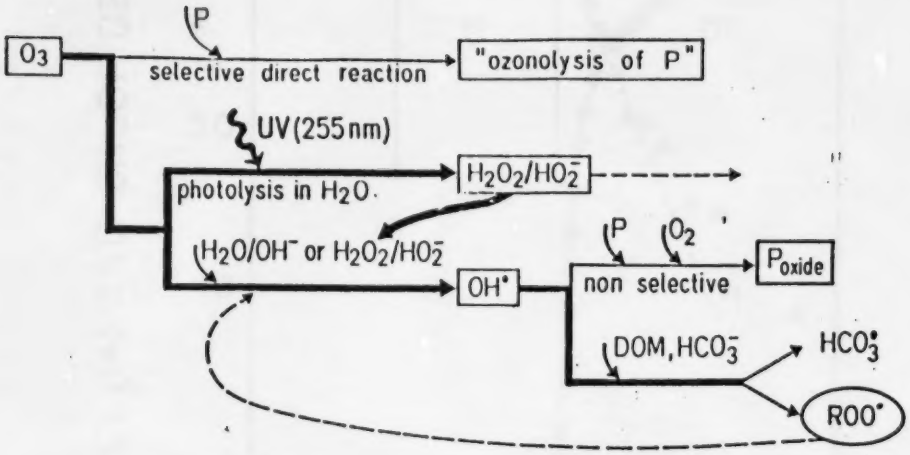

Figure 2. Mechanisms for reactions between ozone and pollutants (20).

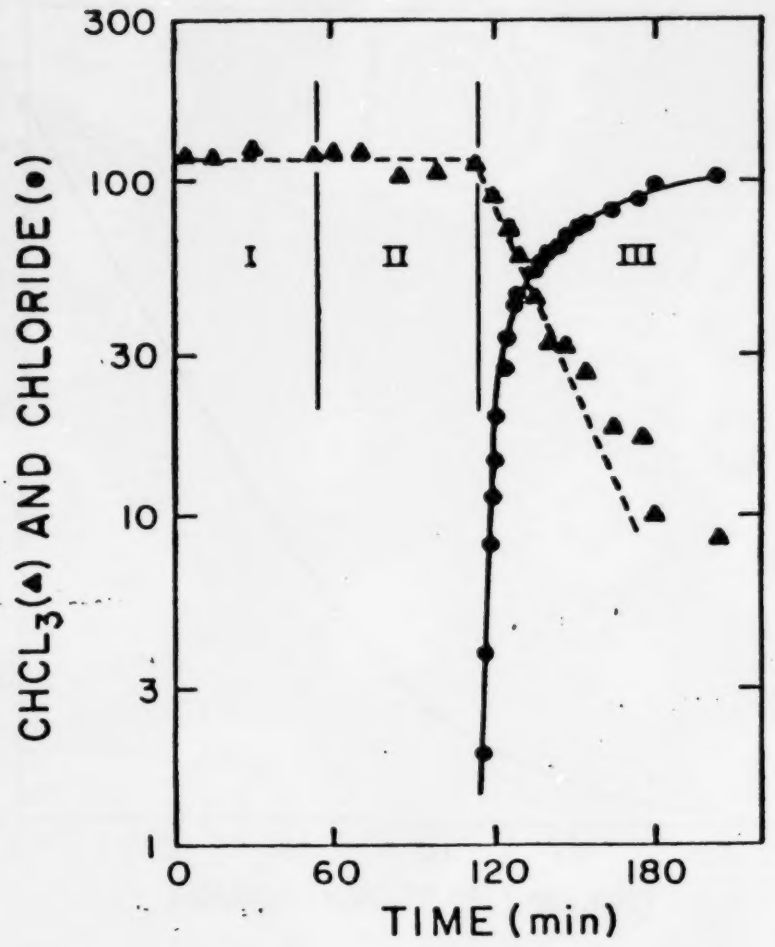

Figure 3. Heterogeneous photocatalysis of the reduction of chloroform (24). Reaction conditions: I, irradiated by blacklight with no titanium dioxide present; II, in dark with titanium dioxide present; III, irradiated by blacklight with titanium dioxide present (24).

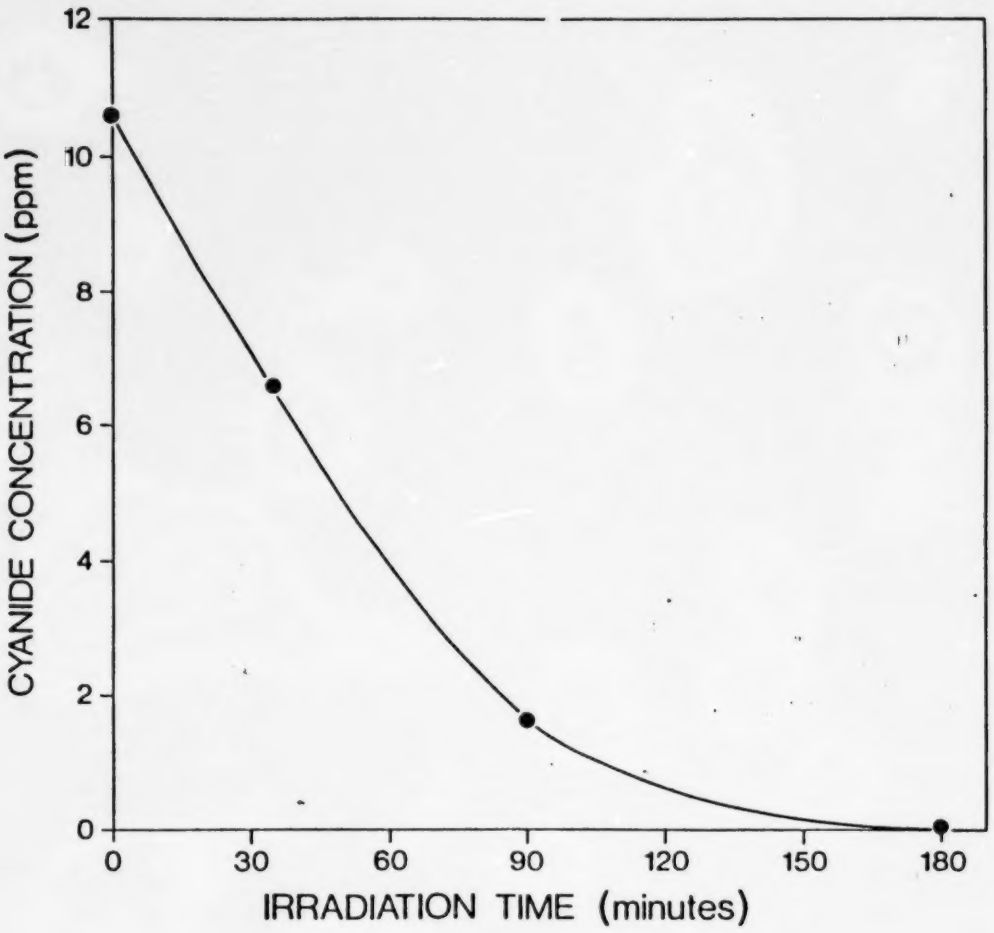

Figure 4. Photocatalyzed reaction of cyanide (28).